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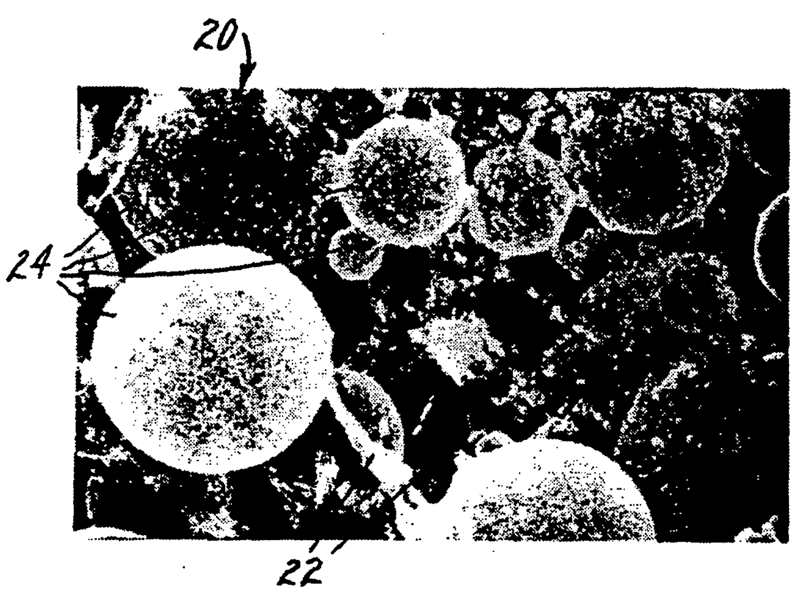

(57) Abstract

A composite article comprising, in the unexpanded form, a fibrillated polyolefin matrix and energy expandable hollow polymeric particles, which article, on applying energy such as steam, heat or laser energy, provides an expanded article having decreased density. The expanded articles are lightweight, breathable, and efficient thermal insulators. The articles in sheet f rm are thin, and when laminated to or between other fabric material, provide an article that is both a thermal insulator and breathable.

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INSULATING ARTICLES

FIELD OF THE INVENTION

This invention relates to a composite article and a method therefor, the article comprising a fibrillated polymer network having unexpanded or expanded forms of hollow polymeric particles enmeshed therein. The article is useful as a thermal insulator.

BACKGROUND OF THE INVENTION

Composite articles comprising fibrous webs are known.

U.S. Patent No. 4,433,024 describes vapor-sorptive garments having a low insulation value comprising a fibrous web and a permeable support fabric to which may be adhered a film such as microporous polytetrafluoroethylene (PTFE).

U.S. Patent No. 3,962,153 discloses a porous product consisting essentially of expanded, amorphous locked PTFE which can be laminated and impregnated to provide shaped articles. U.S. Patent No. 4,096,227, and related U.S. Patent Nos. 3,953,566 and 4,187,390, relate to a porous expanded PTFE product. The more highly expanded materials of these references can be useful thermal insulators.

U.S. Patent No. 4,168,298 describes a process for fibrillated PTFE yarn and felts useful for fireproof or protective clothing.

The background art taught several formulations for blending an aqueous PTFE dispersion with various additives and/or adjuvants designed for specific purposes. For example, U.S. Patent No. 4,460,642 discloses a water-swellable composite sheet of PTFE microfibers and hydrophilic absorptive particles enmeshed therein which is useful as a wound dressing.

U.S. Patent No. 4,990,544 teaches a gasket comprising a fibrillated PTFE resin and a fine inorganic powder dispersed therein. U.S. Patent No. 4,985,296 teaches an expanded, porous PTFE film containing filler material which is purposely compressed to provide thin films where space reduction is desirable.

Assignee's patent application U.S.S.N. 07/639,515 (now allowed) discloses a method of controlling the porosity in a composite PTFE article by controlling the amount of lubricant incorporated in the article during processing. The article also has controlled mean pore size. Design News, "Particulates Captured/Carried by Fibrillated PTFE", February 9, 1987 (Cahners Publishing Company), discloses particles carried by fibrillated PTFE membranes having a porosity in the range of 30 to 70% and pore sizes from 0.01 to 5.0 microns.

U.S. Patent Nos. 4,971,736, 4,906,378, and 4,810,381 disclose a composite chromatographic sheet-like article and method therefor. The article comprises a PTFE fibril matrix and non-swellable sorptive hydrophobic particles enmeshed in the matrix. References cited in these patents relate to other PTFE matrices containing particulates. U.S. Patent No. 4,971,697 teaches a chromatographic article comprising a PTFE fibril matrix having enmeshed therein a mixture of non-swellable sorptive particles and hydrated silica flakes. Hagen, et al., "Membrane Approach to Solid Phase Extractions", Analytica Chimica Acta, 236 (1990) 157-164, relates to particle loaded fibrillated PTFE matrices useful in extraction applications.

U.S. Patent No. 4,923,737 discloses a method for a "metal cloth" prepared from fibrillated PTFE containing metal or other particles entrapped in the fibrils.

In regard to polymers, fibrillated PTFE has also been combined with a polyamide to provide articles by extrusion blow-molding (U.S. Patent No. 4,966,941) and with an elastomer to provide articles with incr ased

durability (U.S. Patent No. 4,962,136). U.S. Patent No. 4,945,125 t aches a process of producing a fibrillated semi-interpenetrating polymer network of PTFE and silicone elastomer. U.S. Patent No. 4,914,156 describes a blow moldable composition comprising a polyether, an epoxide polymer, a source of catalytic cations, and fibrillatable PTFE. U.S. Patent No. 4,902,747 discloses a polyarylate composition containing fibrillatable PTFE.

U.S. Patent Nos. 4,199,628 and 4,265,952 relate to a vermicular expanded graphite composite blended with a corrosion resistant resin such as PTFE with improved impermeability to corrosive fluids at high temperatures.

U.S. Patent No. 4,483,889 discloses a method of making a composite material comprising a fibrous matrix, expandable polymeric microbubbles, and a formaldehyde-type resin involving distributing the expandable microspheres (either expanded or unexpanded) into a cellulose fiber matrix, expanding the polymeric bubbles by application of heat (in the case where unexpanded microbubbles were used), and impregnating the resulting porous matrix with a curable formaldehyde-type resin to give a foam which is stated to be useful as a building material.

SUMMARY OF THE INVENTION

Briefly, the present invention provides a composite article comprising

(a) a fibrillated polyolefin matrix, and

(b) energy expandable or expanded hollow polymeric particles enmeshed in the matrix.

The preferred fibrillated polymer network is a polytetrafluoroethylene (PTFE) fibril matrix.

Preferably, the weight ratio of expandable hollow particles to polymer network is in the range of 25:75 to 98:2 percent by weight. Opti nally, the article

further comprises adjuvants, for example colorants or deodorants, in an amount f about 0.01 to about 50 percent by weight based on the total w ight of the composite.

In another aspect, application of energy, e.g., in the form of steam, heat, or laser light, causes expansion of the expandable particles to provide articles, which preferably are membranes (sheet-like articles), that can be useful as thermal insulators.

The energy expanded membrane can be laminated to at least one surface of a provided fabric to provide a composite fabric which can also be used as an insulating composite.

In another aspect, in a preferred embodiment, this invention provides a method for the preparation of the energy expanded article of this invention comprising the steps of:

(a) fibrillating a mixture of a PTFE suspension comprising energy expandable hollow polymeric particles, and optionally comprising adjuvants, to provide an energy expandable article, and

(b) thermally treating with energy the expandable article to provide the expanded article of the invention.

In yet a further aspect, this invention provides a method for preparation of a thermally insulated fabric comprising the steps:

(a) providing an energy expanded membrane of the invention and providing a fabric, and

(b) adhering the expanded membrane to at least one surface of the fabric to provide a thermally insulated fabric.

What the background has not taught but what this invention teaches is a composite article comprising, in an unexpanded form, a fibrillated polyolefin matrix and energy-expandable polymeric particles, which composite, on application of energy such as steam, heat, or laser

energy, provides an expanded article whose porosity is greater than that of the unexpanded form of the article. The expanded articles are lightweight, breathable (up to about 95 percent voids), and efficient thermal insulators. The articles, when in membrane form, are thin, and when laminated to or between other fabric material, provide an article that is both a thermal insulator and breathable.

Assignee's copending patent application, U.S.S.N. 722665 discloses composite sheet-like articles comprising a fibrillated PTFE matrix having sorptive particulate and energy expandable or expanded particulate enmeshed therein, the composite sheet-like articles having controlled interstitial porosity and being useful in separation sciences.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a plan view (magnification of approximately 1000X) of an unexpanded composite article of the invention;

FIG. 2 shows a plan view (magnification of approximately 1000X) of an expanded article of the invention.

DETAILED DESCRIPTION OF THE DRAWING

FIG. 1 shows one embodiment of a composite article 10 of the present invention having PTFE fibrillated matrix 12 in which are enmeshed thermally expandable hollow polymeric particles 14;

FIG. 2 shows expanded article 20 of FIG. 1 of the invention having PTFE fibrillated matrix 22 in which are enmeshed thermally expanded hollow polymeric particles 24.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

In a preferred embodiment, this invention provides a composite membrane which can be used to provide thermal insulation. The composite membrane comprises expandable hollow polymeric microbubbles, referred to as expandable particulate, held within a fibrillated polyolefin network. Optionally, other adjuvants or components can be added to the composite to provide property modification, such as colorants and deodorants, for added utility for the resulting membranes. Upon providing energy in the form of steam or heat (or from a source such as a laser) to the membrane, the expandable particulate is caused to expand which results in both a volume increase and a density decrease of the membrane.

Expandable particulate material useful in the present invention exhibits intumescence upon application of heat and can be swellable or non-swellable in aqueous or organic liquid, and preferably is substantially insoluble in water or organic liquids used in preparation of the composite membranes. In addition, the expandable particulate is not homogeneous, i.e., it is not a uniform bead of polymer but rather comprises a polymeric shell having a central core comprised of a fluid, preferably liquid, material. A further characteristic is that the overall dimensions of the expandable particulate increase upon heating at a specific temperature. This expansion or intumescence is different from expansion due to solvent swelling and can occur in the dry state (i.e., in the absence of solvent).

Expandable particulate includes those materials comprised of a polymeric shell and a core of at least one other material, either liquid or gaseous, most preferably a liquid at room temperature, in which the polymeric shell is essentially insoluble. A liquid

core is advantageous becaus the degree of expansion is directly related to the volume change of the core material at the expansion temperature. For a gaseous core material, the volume expansion expected can be approximated from the general gas laws. However, expandable particulate comprising liquid core material offers the opportunity to provide much larger volume changes, especially in those cases where a phase change takes place, i.e., the liquid volatilizes at or near the expansion temperature. Gaseous core materials include air and nonreactive gases and liquid core materials include organic liquids.

Preferred expandable particulate (also called microspheres, microbubbles, and microballoons) have shells comprising copolymers of vinyl chloride and vinylidene chloride, copolymers of vinyl chloride and acrylonitrile, copolymers of vinylidene chloride and acrylonitrile, and copolymers of styrene and acrylonitrile. Further can be mentioned copolymers of methyl methacrylate containing up to about 20 percent by weight of styrene, copolymers of methyl methacrylate and up to about 50 percent by weight of ethyl methacrylate, and copolymers of methyl methacrylate and up to about 70 percent by weight of orthochlorostyrene.

The unexpanded microspheres contain fluid, preferably volatile liquid, i.e., a blowing agent, which is conventional for microspheres of the type described here. Suitably, the blowing agent is 5 to 30 percent by weight of the microsphere. The microspheres can be added in different manners, as dried particles, wet cakes, or in a suspension, e.g., in an alcohol such as isopropanol. The microspheres can also be added in a pre-expanded form.

The unexpanded particulate desirably is in the size range of from about 0.5 micrometer to about 200 micrometers, preferably from 1 micrometer to 100

micrometers, most preferably from 3 micrometers to 50 micrometers. After expansion, the volume of the expandable particulate increases by a factor of at least 1.5, preferably a factor of at least 5, and most preferably a factor of at least 10, and may even be as high as a factor of about 100.

As an example, Expancel™ polymeric microspheres (Nobel Industries, Sundsvall, Sweden) expand from an approximate diameter of 10 micrometers in the unexpanded form to an approximate diameter of 40 micrometers after expansion. The corresponding volume increase is

$$V_f/V_i = (r_f/r_i)^3 = 4^3,$$

or 64-fold, where V_f and r_f are the final volume and radius of the expandable particulate, respectively, after expansion, and V_i and r_i are the corresponding initial values for the unexpanded particulate.

In a two-component system comprising only expandable particulate and fibrillated polymer, useful amounts of expandable or pre-expanded particulate in the composite membrane range from about 25% to about 98% by weight, preferably from 50% to 97%, and most preferably from 60% to 95%.

Preparation of expandable particulate is normally accomplished by suspension polymerization. A general description of some of the techniques that can be employed and a detailed description of various compositions that are useful as expandable particulate can be found in U.S. Patent No. 3,615,972. A further description of compositions useful as expandable particulate in the present invention is given in U.S. Patent No. 4,483,889.

Examples of commercially available expandable hollow polymeric microspheres useful in the present invention include those made of poly(vinylidene chloride-co-acrylonitrile) such as Expancel™ 820, Expancel™ 642, Expancel™ 551, Expancel™ 461, and

Expancel™ 051 polymeric microspheres. Other commercially available materials having similar constructions and comprising, for example, a shell of methacrylonitrile-acrylonitrile copolymer, available as Micropearl™ F-80K microbubbles (Matsumoto Yushi-Seiyaku Co., Ltd., Japan), are also useful as expandable particulate in the present invention.

A wide variety of blowing or raising agents may be incorporated within the polymerization process. They can be volatile fluid-forming agents such as aliphatic hydrocarbons including ethane, ethylene, propane, propene, butene, isobutene, neopentane, acetylene, hexane, heptane, or mixtures of one or more such aliphatic hydrocarbons preferably having a number average molecular weight of at least 26 and a boiling point at atmospheric pressure about the same temperature range or below the range of the softening point of the resinous material of the polymeric shell when saturated with the particular blowing agent utilized.

Other suitable fluid-forming agents are halocarbons such as fluorotrichloromethane, perfluorobutanes, perfluoropentanes, perfluorohexanes, dichlorodifluoromethane, chlorotrifluoromethane, trichlorotrifluoroethane, heptafluorochlorocyclobutane, and hexafluorodichlorocyclobutane, and tetraalkyl silanes such as tetramethyl silane, trimethylethyl silane, trimethylisopropyl silane, and trimethyl-n-propyl silane, all of which are commercially available.

The shape of the expandable particulate is preferably spherical but is not restricted to spherical, i.e., it may be irregular. Other shapes can easily be envisioned such as urnlike as described in U.S. Patent No. 3,615,972. The shape and orientation of the expandable particulate in the composite membrane determine the anisotropy of the expansion step. Where

essentially spherical particles are used, heating leads to isotropic expansion of the composite, i.e., there is no preferred direction of expansion and all three axes expand uniformly so that the overall shape of the membrane does not change, only its size. Other physical constraints that may have been imposed on the membrane, such as during processing or by anchoring one part of the membrane prior to expansion, may lead to less than perfect isotropic expansion where essentially spherical expandable particulate is used.

As a result of the expansion of the expandable particulate, the volume of the composite membrane increases. The percent volume increase is dependent on a number of factors such as the loading of expandable particulate in the composite and the molecular weight of the polymeric shell of the expandable particulate. For highly loaded systems, i.e., composites with greater than about 75% expandable particulate, the degree of expansion of the article approximates the volume increase of the expandable particulate itself.

The decrease in membrane density is inversely proportional to the volume increase of the membrane. For the example cited above in which the expandable particulate is present in greater than about 75% by weight, after expansion, the membrane's density is approximately 1/64th that of the starting membrane. Membranes having densities after expansion on the order of 0.01-0.02 g/cm^3 are easily prepared. The actual drop in density for a given membrane is a function of the volume percent of expandable particulate present in the composite membrane and the particular expandable polymeric microbubble present.

Polymers useful in the present invention to provide the fibrillated polymer network include polyolefins such as polyethylene, polypropylene, and the like, and most preferably, Teflon™ polytetrafluoroethylene (E.I. Dupont de Nemours, Inc.,

Wilmington, DE). It is important that the fibrillated n twork be tight en ugh to support the enmeshment f the expandable particulate so that the final composite has sufficient structural integrity to be handled. In the present invention, the expandable particulate does not easily dislodge from the final composite, i.e., it does not fall out of the membrane when the membrane is handled. An advantage of a PTFE fibrillated network is that PTFE fibrils are able to flow or draw out as the expandable particulate expands, thereby maintaining the structural integrity of the membrane. In addition, the poor bonding of PTFE to the expandable particulate also allows the fibrils to "slide" from a given microbubble's surface during the expansion step, i.e., there is poor adhesion of the fibrils to the polymeric shell of the microbubble. Other fibrillatable polymers are known to those skilled in the art, although PTFE and PTFE-like polymers are preferable.

The PTFE aqueous dispersion employed in producing the preferred PTFE composite membranes and other articles of this invention is a milky-white aqueous suspension of PTFE particles. Typically, the PTFE aqueous dispersion will contain about 20% to about 70% by weight solids, the major portion of such solids being PTFE particles having a particle size in the range of from about 0.05 micrometers to about 1.5 micrometers. Commercially available PTFE aqueous dispersions may contain other ingredients, for example, surfactant materials and stabilizers which promote continued suspension of the PTFE particles. In some applications, it is advantageous to remove the surfactant by extraction or by choosing a PTFE emulsion which is free of surfactant.

Such PTFE aqueous dispersions are commercially available from E.I. Dupont de Nemours, Inc. for example, under the tradenames Teflon™ 30, Teflon™ 30B, or Teflon™ 42, or from ICI, Exton, PA, under the

tradename Flu n™. Teflon 30 and 30B dispersions f PTFE contain about 59% to about 61% solids by weight which are for the most part 0.05 micrometer to 5.0 micrometer PTFE particles and from about 5.5% to about 6.5% by weight (based on weight of PTFE resin) of non-ionic wetting agent, typically octylphenol polyoxyethylene or nonylphenol polyoxyethylene. Teflon 42 dispersions contain about 32% to 35% by weight solids and no wetting agent.

The composite articles of the invention can be provided by the method described in any of U.S. Patent Nos. 4,971,736, 4,906,378, and 4,810,381. Particulate used to prepare composite articles can be pre-expanded or energy expandable. In all cases, processing takes place below the temperature for expansion of the expandable particulate. This processing temperature preferably is room temperature.

The useful range of fibrillated polymer in the final composites can be from about 2% to about 75% by weight, preferably from 3% to 50%, and most preferably from 5% to 40%, based on the total weight of the composite.

Energy can be provided to the composite article to cause expansion of the expandable particulate by any of a number of means, including thermal energy from a heat source such as an oven, steam, or a heat gun, radiant energy such as that given off by an infrared light bulb and a laser such as a carbon dioxide laser, and other means known to those skilled in the art. Steam is a particularly effective expanding agent.

Useful temperature ranges for the thermal expansion step are dependent on the type of polymer used in the microbubble and on the particular blowing agent used. Typical temperature ranges are from about 20°C to about 200°C, preferably from 50°C to 175°C, most preferably from 70°C to 160°C. Nobel Industries

provides a series of expandable bubbles which xpand at differ nt temperatures.

A more complete description of various polymers and blowing agents can be found in U.S. Patent No. 3,615,972. Further discussion of blowing agents in general can be found in U.S. Patent Nos. 4,640,933 and 4,694,027.

The length of time required for full expansion of the article to occur is dependent on the particular blowing agent, the nature of the polymeric shell of the bubble, and the efficiency of heat transfer to the article. For most microbubbles, about five minutes in a convection oven set at a temperature slightly higher than the softening point of the polymeric shell is sufficient to allow full expansion. In cases where heat transfer to the article is much more efficient, such as with the use of steam as a heat source, expansion can occur much more quickly, generally in less than 30 seconds. Similarly, when a pulsed carbon dioxide laser is used to generate localized hot spots in the article, expansion occurs virtually instantaneously in the irradiated areas. It is also possible to only partially expand the microbubbles by controlling the length of time the composite article is exposed to the expansion temperature or exposing the article to a temperature below the normal expansion temperature of the microbubbles such that individual microbubbles have only expanded to a fraction of their potential volume. In this way, the final volume and density of the article can be controlled, in those cases where this is desirable.

Care must be taken to avoid over-exposure of the composite membrane to elevated temperatures since the blowing agent can be driven from the interior of the polymeric microbubble faster than air can permeate into the interior to maintain constant internal pressure, thus causing a collapse of the structure. C nditions

for expansion f expandable particulate vary depending up n the xpandable particulate used and the degree of expansion desired.

Thickness of the membrane prior to expansion can range from about 0.0127 cm to about 0.32 cm, preferably from 0.018 cm to 0.25 cm, most preferably from 0.025 cm to 0.127 cm. When too thin a membrane is made, it has very little structural integrity and is unsuitable for providing useful insulation while membranes having thicknesses outside of the given range may be difficult to form. Thickness after expansion is dependent on several factors, as stated above. Where only expandable polymeric microspheres are present in the fibrillated polyolefin network, thickness after expansion can increase by a factor of at least about 1.5, preferably a factor of at least 2, even as much as a factor of about 4. Thinner membranes can be made by densification as is described in U.S. Patent No. 4,985,286. Alternatively, densification can be accomplished by solvent extraction of the polymeric microspheres.

Other components or adjuvants can optionally be added to the composite membrane to impart some added functionality such as color or utility to the final composite. When present, they can be included in an amount from about 0.01% to about 50% by weight, preferably from 0.1% to 40%, and most preferably from 1% to 25%, based on the total weight of the composite. As with the expandable particulate, the additional component(s) can be swellable or non-swellable in aqueous or organic liquid, and preferably is (are) substantially insoluble in water or organic liquids.

Optional adjuvants can be in the size range of from about 0.1 micrometer to about 600 micrometers, preferably from 1 micrometer to 200 micrometers, most preferably from 5 micrometers to 100 micrometers. This size range is desirable in order to obtain the best

physical properties such as toughness and unif rmity for the resulting membrane.

Examples of fillers that can be included as adjuvants with the expandable polymeric microspheres and the fibrillated polymer network are solid glass beads and hollow glass microbubbles such as C15/250™ and S60/10,000™ microbubbles (3M, St. Paul, MN), and Q-Cel™ 100 and Q-Cel™ 500 microbubbles (PQ Corp., Valley Forge, PA). These are considered inert fillers that can impart added flexibility to the membrane. Other ingredients may be added to impart property modification or added utility of the membrane such as copper phthalocyanine to impart color or to provide deodorizing properties.

It is also within the scope of the invention to include up to 50 weight percent of the total membrane of an elastomeric material such as silicone as described in U.S. Patent No. 4,945,125 to increase the tensile strength of the expanded membrane.

In composites comprised of more than two components, i.e., expandable particulate, fibrillated polyolefin, and at least one other adjuvant, the amount of expandable particulate in the composite may range from greater than 25% to about 98% by weight, more preferably from 40% to 95% by weight, and most preferably from 50% to 90% by weight, based on the total weight of the composite.

The accompanying volume changes of composite articles comprising at least one optional adjuvant in addition to the expandable particulate and the fibrillating polymer can range from less than about 2-fold to greater than 10-fold, or even as high as about 100-fold, again depending on the percent expandable particulate present in the composite and the nature of the composition of the expandable particulate. As noted above, a corresponding decrease in the composite

density will occur as a result of the expansion of the expandable particulate in the composite.

Breathable insulating membranes of the invention are useful thermal insulators for clothing, including footwear, and can be used in building materials, gasket materials, as reinforcing membranes, and as buoyant insulating materials such as life jackets.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percents are by weight unless otherwise stated.

Example 1:

This example describes the preparation of a PTFE membrane incorporating preexpanded polymeric microbubbles into a composite.

Five grams of Expancel 551DE (DE means "dry expanded") preexpanded microbubbles were blended with a mix of 8.7 grams of a 60% by weight dispersion of PTFE in water (Teflon 30B) and 5 grams of a 50:50 by weight isopropanol/H_2O solution. The mix was kneaded until a doughlike consistency was obtained. This was then subjected to a two roll mill set at a 0.51 centimeter gap width for a total of ten initial passes, folding the membrane and turning it 90° after each pass in order to maximize the extent of fibrillation. The gap between the rollers was then decreased incrementally from 0.51 centimeters to 0.0635 centimeters and the web passed through once at each setting. The resulting web was then refolded, the ends removed in order to obtain a folded web having uniform thickness, then the web was subjected to another series of passes on the roll mill with an initial gap of 0.51 centimeters, again decreasing the roller gap after each pass, until a

final thickness of 0.030 centimeters was obtain d. The total number of passes was 22. The resulting membrane had a PTFE content of 51%. After air drying, the web was found to have a smooth texture, was water repellent, and tore easily when subjected to axial elongation. Additional details of the process are given in U.S. Patent No. 4,810,381.

Example 2:

This example describes the preparation of a PTFE membrane incorporating unexpanded polymeric microbubbles into a composite.

Twenty-five grams of Expancel 551DU (DU means "dry unexpanded") polymeric microbubbles were hand blended with a dispersion made by mixing 29.87 grams of a Fluon PTFE dispersion (25% solids) with 10 grams of a 50:50 isopropanol/H_2O solution to give the starting material for a final membrane having 23% by weight PTFE. The mix was kneaded until a doughlike consistency was obtained. This was then subjected to a work up analogous to the procedure given in Example 1. The final web had a thickness of 0.030 centimeters and, after air drying, had a smooth texture, was water repellent, and tore easily when subjected to axial elongation.

Example 3:

This example describes the expansion of a PTFE membrane incorporating unexpanded polymeric microbubbles by application of heat.

A circular disc having a 2.54 centimeter diameter was cut from the membrane of Example 2 using a stainless steel die. The disc was then placed on a rack in a convection oven operating at 120°C. After five minutes, the disk was removed. The circular shape had become more oval by heating. Furthermore, the overall dimensions had increased to 9.53 x 6.99

centimeters x 1.02 millimeters after expansion. The composite membrane had a foamed appearance; a soft, smooth texture; repelled water; and showed good compressibility. In addition, it was noticeably lighter than conventional foams with an approximate density of 0.015 grams per cubic centimeter. The ellipsoidal shape of the expanded web was explained by constraints imposed during the preparation of the membrane, i.e., the web had greater freedom to expand crossweb versus downweb, thus introducing some anisotropy in the PTFE network.

Example 4:

This example describes the preparation of an insulated fabric.

A 50 x 50 cm square cut from the product from Example 2, expanded using the procedure of Example 3, was laminated between two pieces of tricot fabric by application of a thin layer of spray adhesive (3M Super 77™ Spray Adhesive, 3M, St. Paul, MN) to the edges of the tricot and pressing the tacky edges onto the surfaces of the membrane of the invention. The resulting insulated fabric was significantly stronger than the bare membrane.

Example 5:

This example describes the use of steam to cause expansion of the membranes.

When a 2.54 cm disc cut from the membrane of Example 2 was placed in the chamber of an Amsco Vacamatic™ Model 2013 (American Sterilizer Co., Erie, PA) operating at 132°C and 29 torr, the membrane was found to have expanded and recollapsed within 60 seconds. The collapse was due to over-exposure to elevated temperature. Shorter exposure to steam provides the expanded article.

Example 6:

This example describes the xpansi n of a PTFE membrane incorporating unexpanded polymeric microbubbles using laser irradiation.

A sample of the membrane of Example 2 was exposed to the output of a Model 580 CO_2 laser, Apollo Lasers Inc., operating at 10.6 micrometers in either a continuous (CW) or a pulsed mode. The CW mode operated at 20 W and the pulsed mode produced a single 1 millisecond duration pulse with an energy of approximately 100 millijoules. The laser beam was focused on the sample to a spot ranging from 2-5 millimeters in diameter. Linearly treated areas were created by scanning the sample under the laser beam at a rate of 762 centimeters per minute. Expansion occurred in the exposed areas to provide a raised image. When a pulsed mode was used and the sample traversed by the beam, a raised image similar in appearance to Braille writing was obtained.

Example 7:

This example describes the preparation of a PTFE membrane incorporating unexpanded polymeric microbubbles in which the polymeric microbubbles were provided in the form of a wet cake.

One thousand two hundred and forty-two grams of Expancel 551WU (64.9% solids) (WU means wet unexpanded) microbubbles were mixed with 1196 grams of Fluon PTFE dispersion (25% solids) for 6 minutes on high speed using a Ross Mixer™ (Aling Lander Co., Cheshire, CT). After working the doughlike mass as in Example 2, a membrane having 27 weight percent PTFE and a thickness of 0.36 mm was obtained. Samples of the resulting membrane were expanded by heating at 120°C for 3 minutes. The thickness of the expanded sample was 0.10 cm.

Example 8:

This example demonstrates the breathability of the membranes of the invention.

A 7.2 cm disc was cut from the expanded membrane of Example 7 and used in an evaluation for Moisture Vapor Transmission ASTM standard E96-80. The Moisture Vapor Transmission Rate was found to be greater than 700 g H_2O/m^2/24 hrs.

Example 9:

This example demonstrates the insulating ability of the membranes of the invention.

A 25 x 25 cm sample cut from the expanded membrane of Example 7 was used in an apparatus designed to measure the thermal properties of membranes. The Rapid-K™ equipment (Dynatech Scientific, Inc., Cambridge, MA) used a plate-sample-plate configuration to measure heat transmission from a plate at an elevated temperature to a plate at a lower temperature. The results were compared to a National Bureau of Standards Fiberglass Standard Reference Material (SRM). The Clo/(Kg/m^2), which is a measure of the thermal weight efficiency, was found to be between 7.6 and 10.0 for a number of samples whereas for the SRM, the value was 1.46. This shows the superior insulating efficiency of composite membranes of the invention compared to the fiberglass standard.

Example 10:

This example describes the preparation of a PTFE membrane incorporating poly(methacrylonitrile-co-acrylonitrile) expandable microspheres.

Twenty-five grams of Micropearl 80K expandable microspheres were mixed with a dispersion of 29.87 grams of Fluon PTFE dispersion (25% solids) in 10 grams of 50:50 by volume isopropanol/H_2O. The mixture was worked using the procedure of Exampl 2 to provide a

final membrane having a thickness f 0.30 millimeters. The surface of the air dried membrane was noticeably coarser than that of the membranes using poly(vinylidene chloride-co-acrylonitrile) expandable hollow microbubbles.

Example 11:

This example describes the expansion of a membrane containing poly(methacrylonitrile-co-acrylonitrile) expandable microspheres.

The membrane of Example 10 was placed in a convection oven set at 150°C for three minutes. When removed from the oven, the membrane thickness had increased to 1.02 millimeters. The texture was not as rough as the starting membrane. The material had a foamed appearance and was useful as an insulating material.

Example 12:

This example describes the preparation of a membrane having 20% PTFE in the final composite.

Fifty grams of Expancel 551DU microspheres were mixed with a slurry formed by mixing 44.8 grams Fluon PTFE dispersion (27% solids) and 25 grams of a 50:50 by volume solution of isopropanol and water. After fourteen initial passes through a two-roll mill and taking the membrane down twice at successively narrower gap widths using the procedure of Example 2, a membrane containing 20% PTFE was obtained which showed good expansion after heating but had less strength than membranes containing a higher percent PTFE.

Example 13:

This example describes a membrane containing an adjuvant particle as a third component.

Twenty-five grams of glass beads and 25 g of Expancel 551DU microspheres were mixed with a slurry formed by mixing 44.8 grams Fluon PTFE dispersion (27% solids) and 15 grams of a 50:50 by volume solution of isopropanol and water. After fourteen initial passes through a two-roll mill and taking the membrane down twice at successively narrower gap widths using the procedure of Example 12, a membrane containing 20% PTFE was obtained which showed good expansion after heating.

Example 14:

This example describes porosity and percent voids in an article of the invention both before and after expansion.

An article was made from 50 g Expancel 551DU and 34 g Fluon PTFE dispersion (60% solids) by the method of Example 2. A portion of the article was expanded at 140°C for two minutes. Two 47 mm diameter discs were cut, one from the unexpanded and the other from the expanded article, having weights of 0.59 g and 0.044 g,

respectiv ly. The thickness of the unexpand d disc was 0.406 mm; th expanded disc had a thickness of 1.80 mm. The porosity of the discs was measured on a Coulter Porometer II™ (Coulter Electronics, Ltd., Luton, England). The disc cut from the unexpanded article had a minimum pore size of 0.114 micrometer and a maximum pore size of 0.366 micrometer. The expanded disc showed a minimum pore size of 1.650 micrometers and a maximum pore size of 6.330 micrometers (average of two runs). The calculated % voids, using densities of 2.2 g/cm^3 for PTFE, 1.3 g/cm^3 for unexpanded Expancel microspheres, and 0.036 g/cm^3 for the expanded microspheres, were 51.5% before expansion and 76.1% after expansion. This example demonstrates the large increase in porosity and percent voids observed in the articles as a result of expansion.

__Example 15:__

This example describes use of a heat expandable strip cut from a membrane to provide an insulating seal between two pieces of tubing having different diameters.

A 7 millimeter wide and 5 centimeter long strip of a 0.030 centimeter thick membrane containing 75% Expancel 551DU microbubbles and 25% PTFE, prepared using the method of Example 2, was wrapped around a 1 centimeter long length of a stainless steel tube having a 7 millimeter outer diameter. The wrapped portion of the tube was then inserted into the end of a second tube having a 10.3 millimeter inner diameter. The fit was loose so that the wrapped inner tube would easily fall out of the second tube if not secured. The entire assembly was then heated in an oven at 120°C for 10 minutes. When removed from the oven, the inner tube was secured in place inside the outer tube by the force exerted from the expansion of the wound strip. Excess strip protruding from the end of the outer tub was

easily removed by rubbing to give a finished, aesthetic appearance to the seal. The expand d strip provided a useful insulator for the inner tube. A sheet-like article of the invention can serve as a useful insulator between any two supports capable of withstanding the expansion temperature.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims:

1. A composite article comprising
   (a) a fibrillated polyolefin matrix, and
   (b) energy expandable or expanded hollow polymeric particles enmeshed in the matrix.

2. The article according to claim 1 wherein said fibrillated polyolefin matrix is a polytetrafluoroethylene matrix.

3. The article according to claims 1 or 2 wherein the weight ratio of expandable hollow polymeric particles to polyolefin matrix is in the range of 25:75 to 98:2 percent by weight.

4. The article according to claims 1 to 3 further comprising adjuvants in the amount of about 0.01 to about 50 percent by weight based on the total weight of the composite.

5. The article according to claims 1 to 4 wherein said hollow particles comprise a fluid core and a polymeric shell.

6. The article according to claim 1 to 5 further comprising more than 0 and up to 50 weight percent of an elastomeric material.

7. An energetically expanded article according to claims 1 to 6.

8. The article according to claims 1 to 7 which is at least one of a sheet-like article and a thermal insulator.

9. A composite article c mprising th energetically expanded article according to claim 7 laminated to at least one side f a provided fabric, or which is an insulating seal between two substrates.

10. A method for preparing an energetically expandable article according to claims 1 to 7 comprising the steps:

a) providing an admixture of a fibrillatable PTFE aqueous dispersion and energetically expandable hollow polymeric particles, and optionally adjuvants,

b) fibrillating the mixture of a) to provide an energetically expandable article,

c) optionally, energetically treating the article from b) to provide an expanded article of the invention, and

d) optionally, providing a fabric and adhering the expanded article to the fabric to provide an insulating article.

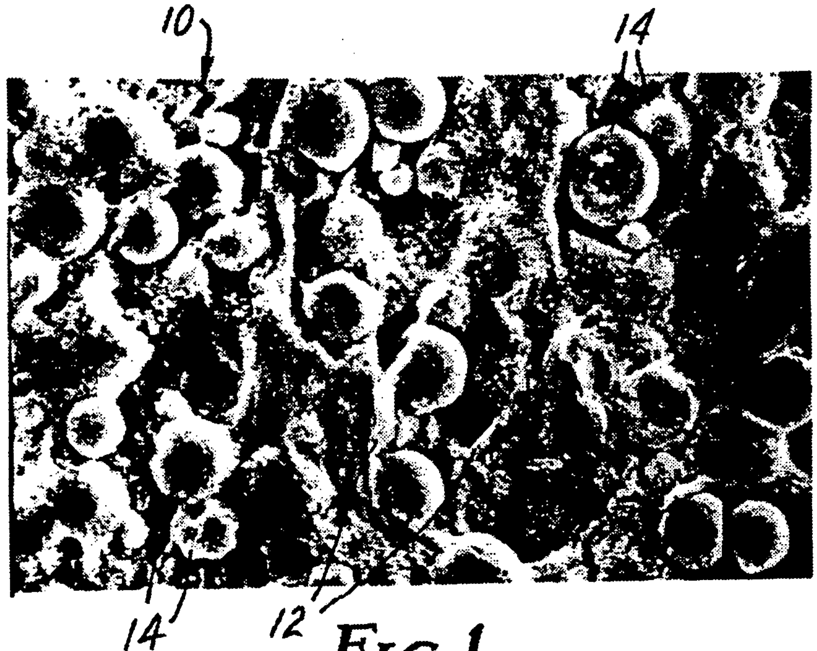

FIG.1

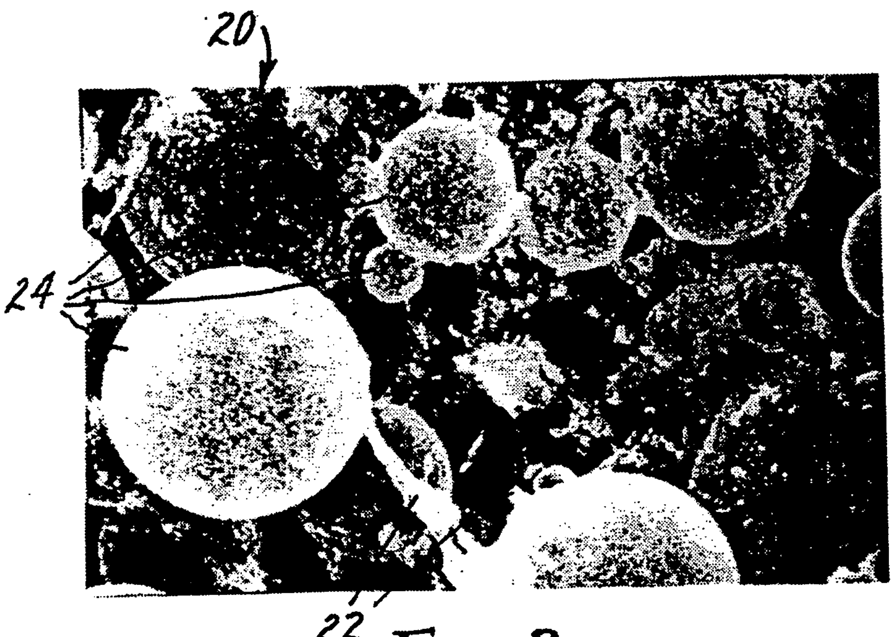

FIG.2

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/04122

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 J 5/18,C 08 J 9/32,B 32 B 27/02,B 32 B 27/12, B 32 B 27/18,B 32 B 5/26,B 32 B 5/30

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System	Classification Symbols
IPC5	C 08 J,B 32 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	US, A, 4 483 889 (ANDERSSON) 20 November 1984 (20.11.84), see claims; column 2, line 58 - column 3, line 20 (cited in the application). --	1,3-5, 7,8,10
Y	DESIGN NEWS, 9 February 1987, Cahners Publishing Company, B.J. HOGAN "Particulates captured/carried by fibrillated PTFE", pages 166-167 see pages 166-167 (cited in the application). --	1-3,8, 10
A	GB, A, 1 603 635 (TULLIS RUSSEL & COMPANY LIMITED) 25 November 1981 (25.11.81), see claims 1,11,13,14; page 1, lines 31-40. ----	1

* Special categories of cited documents:

"A" document defini[illegible] the general state of the art which is not considered to b[illegible] particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
25 September 1992	19 OCT 1992
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	WEIGERSTORFER e.h.

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 92/04122 SAE 61671

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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